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(30) Priority Data: 96200715.9 15 March 1996 (15.03.96) (34) Countries for which the regional or international application was filed: (71) Applicant (for all designated States except AU BB CA KE LK LS MN MW NZ SD SG SZ TT UG): UNI N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdar (71) Applicant (for AU BB CA GB IE KE LK LS MN MW SG SZ TT UG only): UNILEVER PLC [GB/GB]; UNILE	ILEVERM (NL) NZ SI Unileve Lever laarsser Lever laarssen Lever laarssen Lever	LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: CLEANING GELS

(57) Abstract

The invention relates to a cleaner concentrate composition which can be diluted to form a viscous use solution, the cleaner composition comprising: an ammonium compound and/or an amphoteric compound and an anionic surfactant, wherein the composition is free of amine oxide.

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CLEANING GELS

Field of the invention

The present invention concerns cleaning compositions, and more specifically cleaning compositions which can be diluted in order to provide cleaning gels.

Background of the invention

For the cleaning of hard surfaces and objects, particularly in industrial, institutional and catering environments,

10 cleaning products in the form of gels, which have a prolonged contact with the target surface to be cleaned, are known.

A problem with known gels is that they comprise amine oxide as a gelling agent, which is environmentally harmful, for example by forming nitrosoamines.

An object of the present invention is to yield a gel cleaner, free of amine oxide.

The inventors have surprisingly found that said object can be achieved by applying an ammonium compound, preferably a quaternay or a ternary ammonium compound instead of amine oxide as a gelling agent, and that said ammonium compound can be used to yield an effective cleaning gel.

Definition of the invention

- According to a first aspect of the present invention, there is provided a cleaner concentrate composition which can be diluted to form a viscous use solution, the cleaner composition comprising:
- an ammonium compound and/or an amphoteric compound; and
 an anionic surfactant, wherein the composition is free of amine oxide.

Since this cleaner composition is free of amine oxide, environmentally harmful effects are reduced.

A second aspect of the present invention provides a cleaning method comprising the steps of diluting a

concentrate composition according to the invention with water to a concentration to yield a desired viscosity and applying the composition thus diluted to a target surface. Further aspects of the present invention provide a cleaning gel obtainable by diluting with water the concentrate composition of the invention, and the use of said cleaning gel for cleaning target surfaces.

Detailed description of the invention

10 When in use for cleaning a surface, the cleaner concentrate composition of the present invention is desirably diluted with water to a concentration of from 1 to 20%, preferably from 2 to 10%, by weight, so as to yield a cleaning gel having a suitable viscosity. Particularly when cleaning verticle surfaces, said cleaning gel should have sufficient viscosity for obtaining effective cleaning performance.

The ammonium compound present in the composition of the invention is effectively a quaternary or a ternary ammonium compound. More preferably, said ammonium compound is selected from the group consisting essentially of benzalkonium chloride and primary, secondary or tertiary amines (C12-C27).

If a quaternary ammonium compound is used, it has desirably a chain length of C8-C20, preferably C12-C16.

A tertiary amine is effectively present for obtaining viscous use solution having a pH-value of 9.5-10, whereas a secondary amine is suitably used when a viscous use solution having a pH of 3.5-4.0 is needed.

- The ammonium compound is preferably present at a concentration of from 1 to 25%, more preferably from 1 to 10%, by weight of the concentrate composition of the invention.
- 35 Preferably, the anionic surfactant present in the concentrate composition of the invention consists one or

more fatty acids neutralised by an alkaline source, preferably an alkaline metal salt such as a sodium salt, these forming a soap. Effectively, said anionic surfactant includes saturated and unsaturated fatty acids in a weight ratio of 1:5, preferably 1:2. Preferably, the fatty acids are selected from the group consisting essentially of oleic acid, palmitic acid, caprylic acid and isostearic acid. The alkaline source is preferably present in the concentrate composition of the invention at a concentration of 5 to 40% by eight.

Desirably, the concentrate composition of the present invention further comprises a cleaning agent selected from the group consisting of a secondary alkane sulphonate, an alkane sulphate, an ether sulphate, and mixtures thereof. More preferably, the concentrate composition of the invention includes a secondary alkane sulphonate at a concentration of from 1 to 25% by weight.

In order to boost the cleaning performance thereof, the concentrate composition of the invention may effectively further comprise a nonionic surfactant.

A suitable further component of the concentrate composition of the invention is a solvent, which can be effectively used for establishing the desired viscosity of the use solution to be obtained from said concentrate by dilution. Said solvent is preferably selected from the group consisting of isopropanol, ethanol, hexylene glycol, propylene glycol, diethylene glycol, monoethyl/butyl ether, dioxitol butyl dioxitol, and mixtures thereof.

A further preferred component of the concentrate composition of the invention is a sequestrant, said sequestrant being desirably present therein at a level of 0.1 to 15% by weight. Said sequestrant is preferably selected from the group consisting of ethylene-diamine-

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tetraacetic acid, nitrilo-tri-acetic acid, citric acid, methyl-glycine-diacetic acid, serine diacetic acid, alkaline salts thereof, and mixtures thereof.

5 The concentrate composition of the invention may effectively further include threshold agents such as phosphonates, polyacrylates and hydrotropes, and/or iron binders such as sodium gluconate. These threshold agents and iron binders may be suitably present at a concentration of from 0.1 to 5% by weight.

The concentrate composition preferably has a flash point of between 25-50°C.

The present invention will now be illustrated by way of the following examples.

Field trials have been carried out with the following embodiments of a composition according to the present invention.

Figures 1-3 show the measured ratio of saturated to unsaturated fatty acids of compositions 1 to 3 respectively.

Composition 1: General purpose liquid detergent for foamgel and gel cleaning (low flash point).

Raw material	% E	as supplied	as 100%
(2) potassium hy	droxide (50%)	12.00	6.00
(3) ethanol		10.00	10.00
(4) palmitic aci	đ	0.75	0.75
(5) oleic acid		5.50	5.50
(6) caprylic aci	d	1.50	1.50
(7) gluconic aci	d Na-salt	0.50	0.50
(8) alkane supho	nic acid		
Na-salt (30%)	1.50	0.30
(9) cumene sulph	onic acid		
Na-salt (40%)	14.00	4.00
(10) alkyl dimeth	yl benzyl		
ammonium chl	oride (50%)	3.00	1.50
(11) ethylene dia	mine tetraacetic		
acid 4 Na-sa	lt (40%)	10.00	4.00
(12) sodium hydro:	xide (50%)	4.00	2.00
(1) water (demine	eralised) up to	100.00	100.0
	(2) potassium hy (3) ethanol (4) palmitic aci (5) oleic acid (6) caprylic aci (7) gluconic aci (8) alkane supho Na-salt (30% (9) cumene sulph Na-salt (40% (10) alkyl dimeth ammonium chl (11) ethylene diamacid 4 Na-sa (12) sodium hydrox	 (2) potassium hydroxide (50%) (3) ethanol (4) palmitic acid (5) oleic acid (6) caprylic acid (7) gluconic acid Na-salt (8) alkane suphonic acid Na-salt (30%) (9) cumene sulphonic acid Na-salt (40%) (10) alkyl dimethyl benzyl ammonium chloride (50%) (11) ethylene diamine tetraacetic acid 4 Na-salt (40%) (12) sodium hydroxide (50%) 	(2) potassium hydroxide (50%) 12.00 (3) ethanol 10.00 (4) palmitic acid 0.75 (5) oleic acid 5.50 (6) caprylic acid 1.50 (7) gluconic acid Na-salt 0.50 (8) alkane suphonic acid Na-salt (30%) 1.50 (9) cumene sulphonic acid Na-salt (40%) 14.00 (10) alkyl dimethyl benzyl ammonium chloride (50%) 3.00 (11) ethylene diamine tetraacetic acid 4 Na-salt (40%) 10.00 (12) sodium hydroxide (50%) 4.00

30 Production method of composition 1

The raw materials were mixed together in the order given in brackets.

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Characteristics of composition 1

Appearance : light yellow coloured clear

viscous liquid

5

Relative density (20°C) : 1.09

Viscosity :

Neat product : 50-100 mPa.s at 21 s⁻¹ (Haake

10 MV1 25°C)

4% solution : >120 mPa.s at 21 s⁻¹ (Haake MV1

25°C)

pH (1% solution) : 12.3 - 12.5

15 Active alkalinity to

pH 8.2 (phenophtalein) : 4.2 - 4.6% as Na_2O

Total alkalinity to

pH 3.6 (methyl orange) : 5.4 - 5.8% as Na₂O

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Composition 2: Heavy duty liquid detergent for foamgel and gel cleaning (low flash point).

5	.	pozne,	
	Raw material %	as supplied	as 100%
	(2) potassium hydroxide (50%)	24.00	12.00
	(3) ethanol	10.00	10.00
	(4) palmitic acid	0.50	0.50
10	(5) oleic acid	5.25	5.25
	(6) caprylic acid	1.50	1.50
	(7) gluconic acid Na-salt	0.50	0.50
	(8) alkane suphonic acid		
	Na-salt (30%)	1.50	0.45
15	(9) cumene sulphonic acid		
	Na-salt (40%)	2.00	0.80
•	(10) alkyl dimethyl benzyl		
	ammonium chloride (50%)	2.25	1.13
	(11) ethylene diamine tetraaceti	c	
20	acid 4 Na-salt (40%)	10.00	4.00
	(12) sodium hydroxide (50%)	6.00	3.00
		·	
	(1) water (demineralised) to	100.00	100.0
25			

Production method of composition 2

The raw materials were mixed together in the order given in brackets. The plant must be suitable for readily foamable products

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Characteristics of composition 2

Appearance : light yellow coloured clear

viscous liquid

5 Relative density (20°C) : 1.13

Viscosity :

Neat product : 50-100 mPa.s at 21 s⁻¹ (Haake

10 MV1 25°C)

4% solution : >120 mPa.s at 21 s⁻¹ (Haake MV1

25°C)

pH (1% solution) : 12.5 - 12.7

15 Active alkalinity to

pH 8.2 (phenophtalein) : 8.0 - 8.5% as Na₂O

Total alkalinity to

pH 3.6 (methyl orange) : 9.2 - 9.6% as Na₂O

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Composition 3: Heavy duty liquid detergent for foamgel and gel cleaning of ovens and smoke chambers (low flash point).

Raw material	% as supplied	as 100%
(2) potassium hydroxide (50%	32.50	16.25
(3) ethanol	10.00	10.00
(4) palmitic acid	0.35	0.35
(5) oleic acid	5.50	5.50
(6) caprylic acid	2.75	2.75
(7) gluconic acid Na-salt	0.50	0.50
(8) alkane suphonic acid		
Na-salt (30%)	1.50	0.45
(9) cumene sulphonic acid		
Na-salt (40%)	1.00	0.40
(10) alkyl dimethyl benzyl		
ammonium chloride (50%)	2.25	1.12
(11) ethylene diamine tetraace	tic	
acid 4 Na-salt (40%)	5.00	2.00
(12) sodium hydroxide (50%)	7.00	3.50
		
(1) water (demineralised) to	100.00	100.0
	 (2) potassium hydroxide (50% (3) ethanol (4) palmitic acid (5) oleic acid (6) caprylic acid (7) gluconic acid Na-salt (8) alkane suphonic acid Na-salt (30%) (9) cumene sulphonic acid Na-salt (40%) (10) alkyl dimethyl benzyl ammonium chloride (50%) (11) ethylene diamine tetraace acid 4 Na-salt (40%) (12) sodium hydroxide (50%) 	(2) potassium hydroxide (50%) 32.50 (3) ethanol 10.00 (4) palmitic acid 0.35 (5) oleic acid 5.50 (6) caprylic acid 2.75 (7) gluconic acid Na-salt 0.50 (8) alkane suphonic acid Na-salt (30%) 1.50 (9) cumene sulphonic acid Na-salt (40%) 1.00 (10) alkyl dimethyl benzyl ammonium chloride (50%) 2.25 (11) ethylene diamine tetraacetic acid 4 Na-salt (40%) 5.00 (12) sodium hydroxide (50%) 7.00

Production method of composition 3

The raw materials were mixed together in the order given in 30 brackets. The plant must be suitable for readily foamable products.

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Characteristics of composition 3

Appearance : light yellow coloured clear

viscous liquid

5

Relative density (20°C) : 1.15

10 Viscosity:

Neat product : 50-100 mPa.s at 21 s⁻¹ (Haake

MV1 25°C)

4% solution : >120 mPa.s at 21 s⁻¹ (Haake MV1

25°C)

15 pH (1% solution) : 12.5 - 12.7

Active alkalinity to

pH 8.2 (phenophtalein) : 9.7 - 10.1% as Na₂O

20 Total alkalinity to

pH 3.6 (methyl orange) : 10.7 - 11.1% as Na₂O

CLAIMS

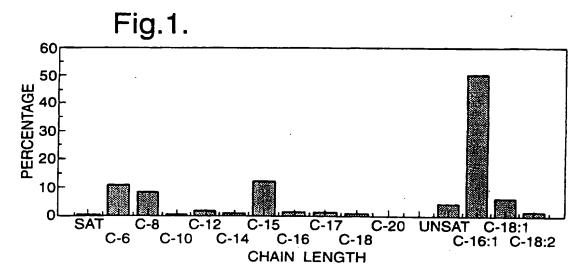
- 1. A cleaner concentrate composition which can be diluted to form a viscous use solution, the cleaner composition comprising:
- an ammonium compound and/or an amphoteric compound; and
 an anionic surfactant,
 wherein the composition is free of amine oxide.
- 2. A composition according to claim 1, which on dilution with water forms 1-20% by weight of a gel.
- 3. A composition according to claim 1 or 2, wherein the ammonium compound is a quaternary or a ternary ammonium compound.
- 4. Composition according to claim 3, wherein the ammonium compound is selected from the group consisting of benzalkonium chloride, primary, secondary or tertiary alkyl amines (C12-C27), and mixtures thereof.
- 5. Composition according to claim 3, comprising 1-25% by weight of the ammonium compound.
- 6. Composition according to claim 3, wherein the quaternary ammonium compound has a chain length of C8 C20, preferably C12 C16.
- 7. Composition according to claim 4, wherein the alkyl amine is tertiary for a pH of 9.5-10.0 and secondary for a pH of 3.5-4.0.
- 8. Composition according to any of the preceding claims, wherein the anionic surfactant consists of one or more

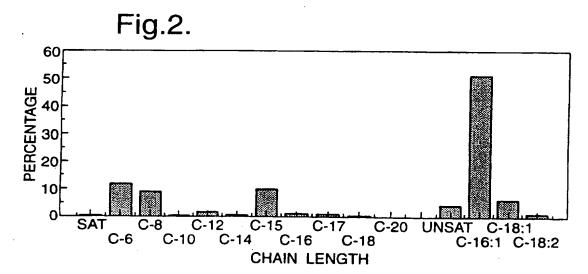
fatty acids neutralized by an alkaline source, these forming a soap.

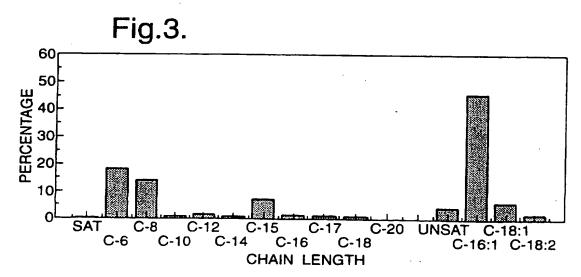
- 9. Composition according to claim 8, wherein the ratio of saturated to unsaturated fatty acids is 1:5, preferably 1:2.
- 10. Composition according to claim 8, wherein the fatty acids are selected from the group consisting of oleic acid, palmitic acid, caprylic acid, iso-stearic acid, and mixtures thereof.
- 11. Composition according to claim 8, wherein the alkaline source comprises 5-40% by weight of the composition.
- 12. Composition according to any of the preceding claims further comprising a cleaning agent selected from the group consisting of a secondary alkane sulphonate, an alkane sulphate, an ether sulphate, and mixtures thereof.
- 13. Composition according to claim 12, wherein the secondary alkane sulphonate is present at a concentration of 1 to 25% by weight of the composition.
- 14. Composition according to any of the preceding claims, further comprising a solvent selected from the group consisting of isopropanol, ethanol, hexylene glycol, propylene glycol, diethylene glycol, mono ethyl/butylether, dioxitol butyldioxitol, and mixtures thereof.
- 15. Composition according to any of the previous claims, having a flash point of between 25-50°C.
- 16. Composition according to any of the preceding claims, further comprising a sequestrant selected from the group consisting of ethylene-diamine-tetraacetic acid, nitrilo-

triacetic acid, citric acid, methylglycine-diacetic acid, serine diacetic acid, alkaline salts thereof, and mixtures thereof.

- 17. Composition according to claim 16, wherein the sequestrants are present at a level of from 0.1 to 15% by weight of the composition.
- 18. Cleaning method, comprising the steps of diluting a composition according to any of the preceding claims with water to a concentration to yield a desired viscosity and applying the composition thus diluted to a target surface.
- 19. A cleaning gel, obtainable by diluting the concentrate composition according to any of claims 1 17.
- 20. The use of a cleaning gel according to claim 19 for cleaning target surfaces.







SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

Inten al Application No PCT/EP 97/01176

A CLAS	SIFICATION OF SUBJECT MATTER		
IPC 6	C11D10/04 C11D1/65 C11D1	/94 C11D17/00	
According	to International Patent Classification (IPC) or to both national	classification and IPC	
	DS SEARCHED		
IPC 6	documentation searched (classification system followed by class C11D	afication symbols)	
Document	ation searched other than minimum documentation to the extent	that such documents are included in the fields	searched
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Electronic	data base consulted during the international search (name of data	a base and, where practical, search terms used))
C. DOCUM	MENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the	be relevant massages	B alamana at i at
ļ 			Relevant to claim No.
Х	WO 94 25561 A (NOVONORDISK AS E November 1994 see claims 1-3,8-10	ET AL.) 10	1,3,8, 10,11
A	CA 1 151 501 A (TASTAYRE GILLES August 1983	S M) 9	1
	see page 13, line 7 - line 8 see claims; examples		
A	US 5 246 629 A (FUKUMOTO YOSHIN 21 September 1993 see the whole document	ORI ET AL)	1
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	er documents are listed in the continuation of box C.	X Patent family members are listed it	n annex.
'A' documei	gories of cited documents: nt defining the general state of the art which is not red to be of particular relevance ocument but published on or after the international	"T" later document published after the inte or priority date and not in conflict wit cited to understand the principle or th invention	h the application but
L' document which is	te It which may throw doubts on priority claim(s) or cited to establish the publication date of another or other special reason (as specified)	"X" document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the	be considered to
O' document other me	it referring to an oral disclosure, use, exhibition or	cannot be considered to involve an inv document is combined with one or mo ments, such combination being obviou in the art.	entive step when the
later tha	n the priority date claimed	'&' document member of the same patent i	amily
Date of the ac	tual completion of the international search	Date of mailing of the international sea	
	June 1997	02.07.97	
lame and ma	iling address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk	Authorized officer	
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INTERNATIONAL SEARCH REPORT

information on patent family members

Interr ial Application No
PCT/EP 97/01176

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9425561 A	10-11-94	AU 6720294 A CA 2162021 A EP 0697037 A JP 8509759 T NO 954401 A	21-11-94 10-11-94 21-02-96 15-10-96 03-11-95
CA 1151501 A	09-08-83	NONE	
US 5246629 A	21-09-93	JP 4085400 A	18-03-92

Form PCT/ISA-210 (patent family annex) (July 1992)